

LA-UR-15-28972

Approved for public release; distribution is unlimited.

Title: Advanced Conductor Development with High Temperature Superconductors

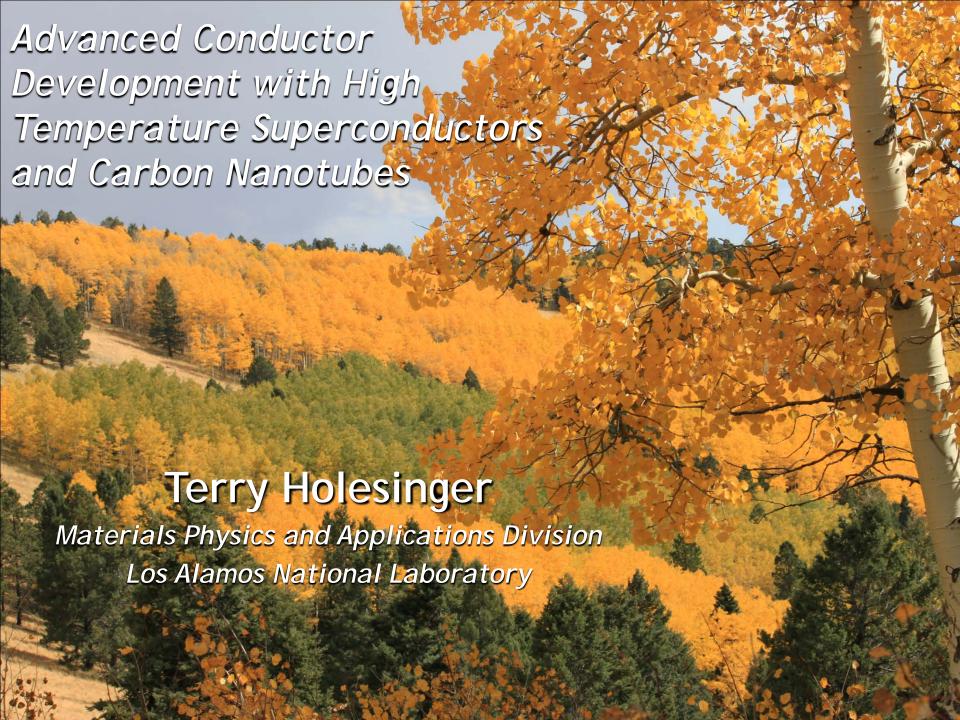
and Carbon Nanotubes

Author(s): Holesinger, Terry George

Intended for: Colloquia at the University of New Mexico

Issued: 2015-11-17





HTS and CNT materials for Next Generation Advanced Conductors.







- Y₁Ba₂Cu₃O_v (YBCO) Coated Conductors
 - HTS Research Perspective:
 - > HTS Industry Perspective:

Part II - Carbon Nanotube Coated Conductors



Research Partnership to Secure Energy for America

- Motivation and Development of CNT Conductors
 - Fabrication Process
 - Composite Wire Performance
- Mesoscale Science and Advanced Conductor Development.



HTS and CNT conductors are potential energy-efficient replacements for conventional copper and aluminum wires.

electricity delivery



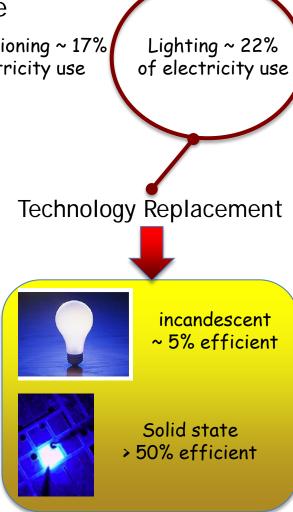
7-10% transmitted energy lost = 40 GW

More power to Urban Centers
Urban restrictions on substations
Enivronmental Concerns:
Contaminating and flammable
transformer oil

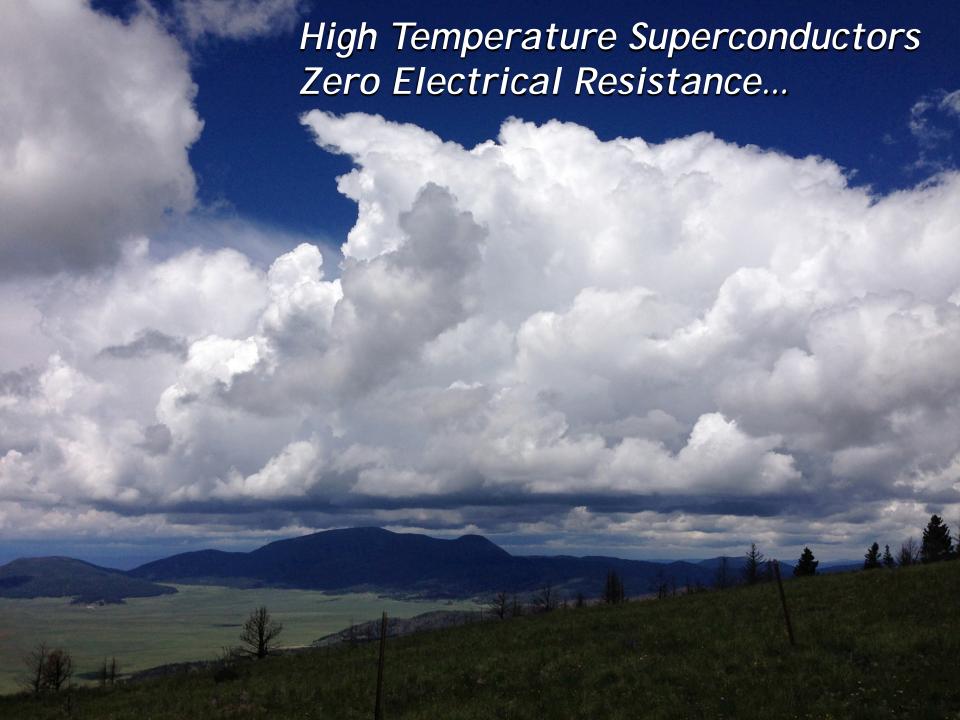
electricity use Air conditioning ~ 17% Flectric motors ~ 25% of electricity use of electricity use Lightweight, durable conductor for electric power systems in weight-sensitive applications











Acknowledgements

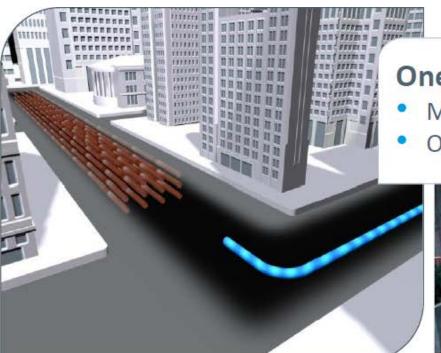
- HTS Coated Conductors Many efforts in different fields of science and engineering.
- ◆ HTS property measurements: B. Maiorov, L. Civale, Matt Feldmann, S.P. Ashworth, J.Y. Coulter, D.N. Nguyen, J.O. Willis
- Synthesis: J.R. Groves, Matt Feldmann, Q.X. Jia, J.L. Driscoll, I. Usov, R.F. DePaula,, P.C. Dowden, J. Rowley, C. Sheehan, S.R. Foltyn (ret.), P.A. Arendt (ret.), and T.G. Holesinger
- Structural Characterization: J.R. Groves, I. Usov, R.F. DePaula, J. Baca, V. Matias, J. Kennison, and T.G. Holesinger
- ◆ Group Leaders: D.E. Peterson (ret.), K.R. Marken (now at DOE-HEP)
- My Role: Synthesis (Powder Synthesis, High Purity Targets, Wire and Film Process Development), Electron Microscopy, and P.I. for the AMSC (industrial) CRADA.

This work was supported by the U.S. Department of Energy, Office of Electricity Delivery and Energy Reliability, as part of a DOE program to develop high temperature superconductors for electric power technologies. Los Alamos National Laboratory is operated for the DOE by Los Alamos National Security, LLC., under contract W-7405-ENG-36



Why HTS? Replacement Conductor for Simplifying Transmission in Urban Areas





One MV HTS Cable can replace:

- Many conventional underground circuits
- Overhead transmission line



oto courtesy Consoli

Demonstration Cables: Long Island Power Authority (LIPA) Project













- Long Island Power Authority –Holbrook Substation
- Electrical Characteristics
 - Design Voltage/Current –138 kV / 2400 A ~ 574 MVA
 - Design Fault Current –51,000 A @ 12 line cycles (200 ms)
- Physical Characteristics
 - Length ~ 600m-HTS Conductor Length
- Hardware Deliverables
 - Three ~600 m Long Phase Conductors
- Six 138kV Outdoor Terminations
- Installation/Commissioning –Spring 2007

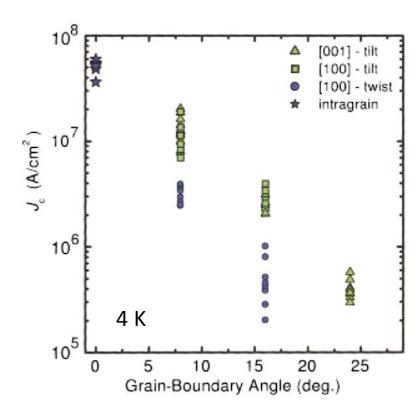
≈ 99 miles of conductor for the 600 m cable



Current HTS Technology (2nd Generation) for Most Applications is based on Y₁Ba₂Cu₃O_v (YBCO) Coated Conductors.

- Why a Coated Conductor? Grain-to-Grain alignment is crucial for high inter-grain J_C.
- Solution: Epitaxial Film Deposition
- Implications for wire:
 - Reliable, large-area epitaxial deposition processes for complex oxides.
 - Flexible, single-crystal-like substrates by the kilometer.

Exponential decrease of J_c with increasing grain boundary angle is observed for most (but not all) YBCO grain boundaries.

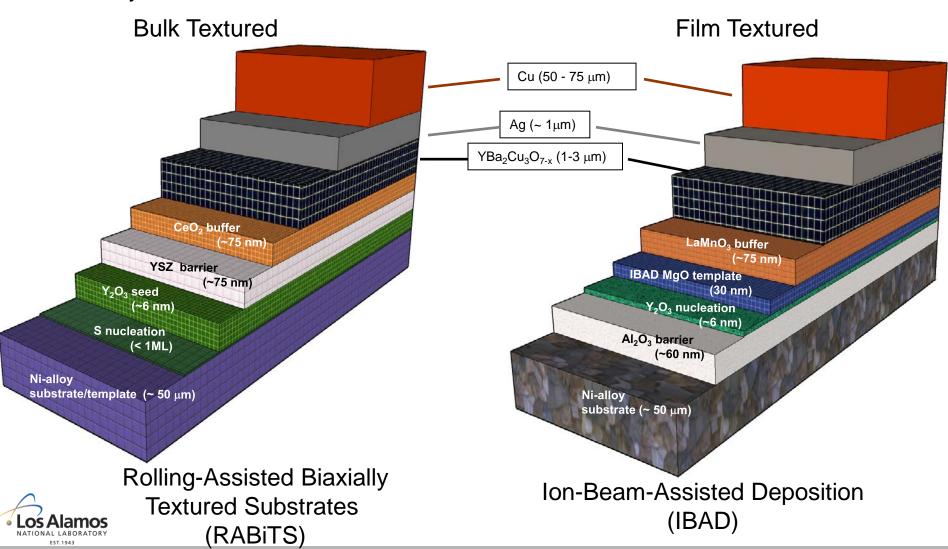


Dimos, D., P. Chaudhari, et al. (1988). "Orientation Dependence of Grain-Boundary Critical Currents in YBa $_2$ Cu $_3$ O $_{7-\partial}$ Bicrystals." Physical Review Letters **61** (2) pp. 219-222.



Coated Conductors are Highly-Engineered Composites

- Two pathways to single-crystal like substrates by the kilometer.
- All the layers in these templates are functionally important.
- HTS layer is around 2% of the total cross sectional area.





Many deposition processes have been adapted for depositing high-J_c YBCO films.

Chemical Solution Deposition

Research:

PLD – Pulsed Laser Deposition

Industry:

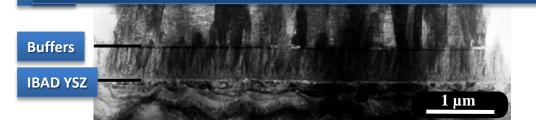
MOD – Metal Organic Deposition

MOCVD Motal Organia





Cross-Cutting: All deposition processes have to produce specifically oriented films and nanoengineered microstructures. (random and correlated defects)

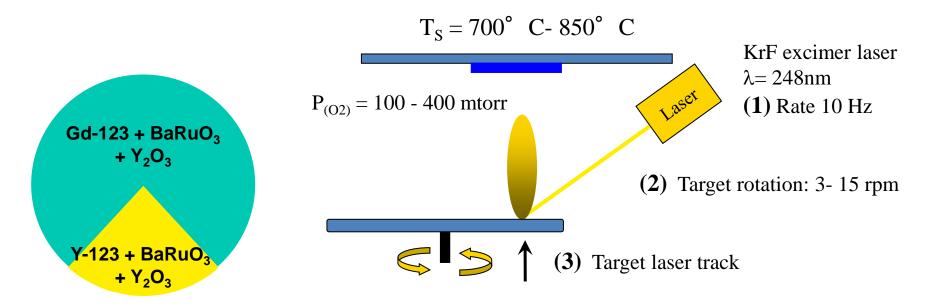


Also columnar MOCVD Co-evaporation



Pulsed Laser Deposition (PLD) is a powerful laboratoryscale film process for complex oxides.

- Near stoichiometric transfer of target composition to film.
- Rapid evaluation of new stoichiometries.
- Epitaxial YBCO films with high critical current densities.
- Ability to tailor the film structure with target modifications.



1/3 : 2/3 Target ratio

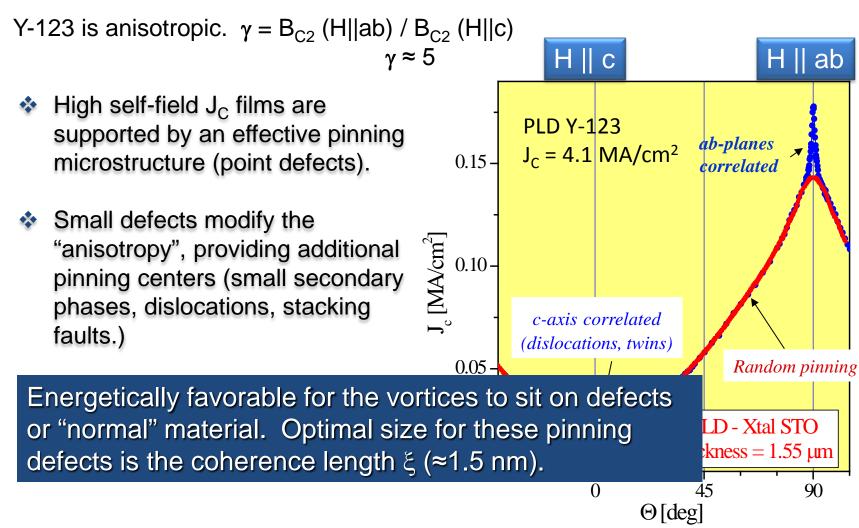
Holesinger - Advanced Conductor Development



Holesinger et al, Advanced Materials 19, 1917-1920, 2007

University of New Mexico - Nov. 2015

High-quality epitaxial YBCO films have high, but anisotropic critical current densities.

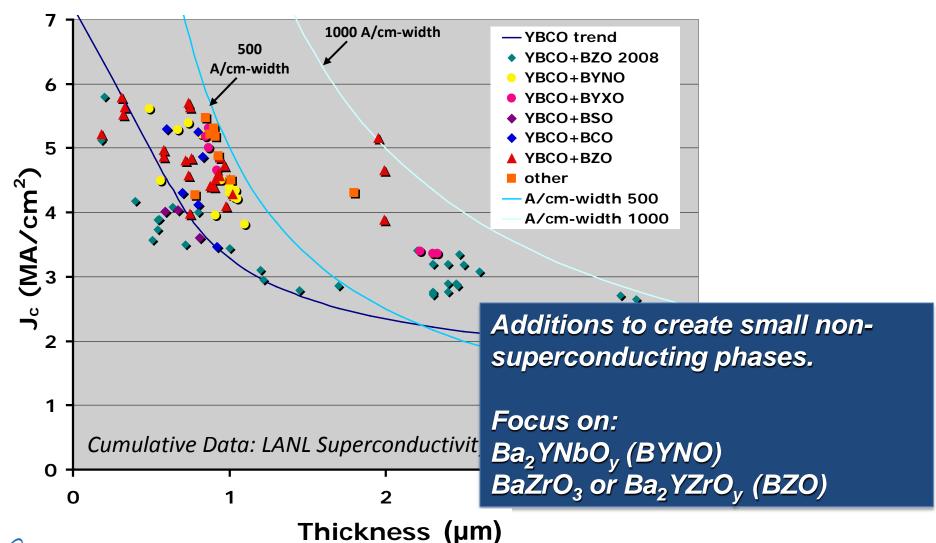




J_C Data and Analysis from Leonardo Civale

University of New Mexico - Nov. 2015

Control of defect structures in research-grade films has led to I_c values up to 1000 A/cm-width.





Film and J_c Data from Matt Feldmann et al

Ba₂YNbO (BYNO)is a double-perovskite that self-assembles as nanorods in PVD films.

Segmented, but continuous rods with amorphous regions around "joints" and changes in tilt.

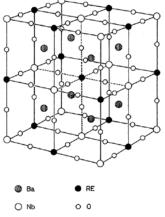
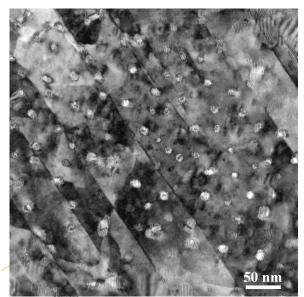
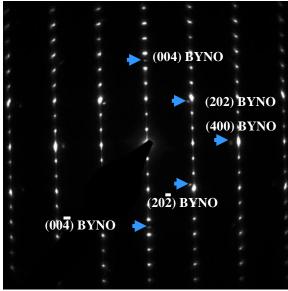
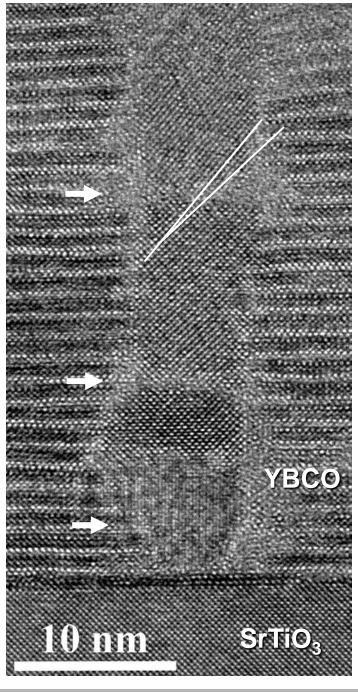


Fig. 2. Crystal structure diagram of REBs. NbO.



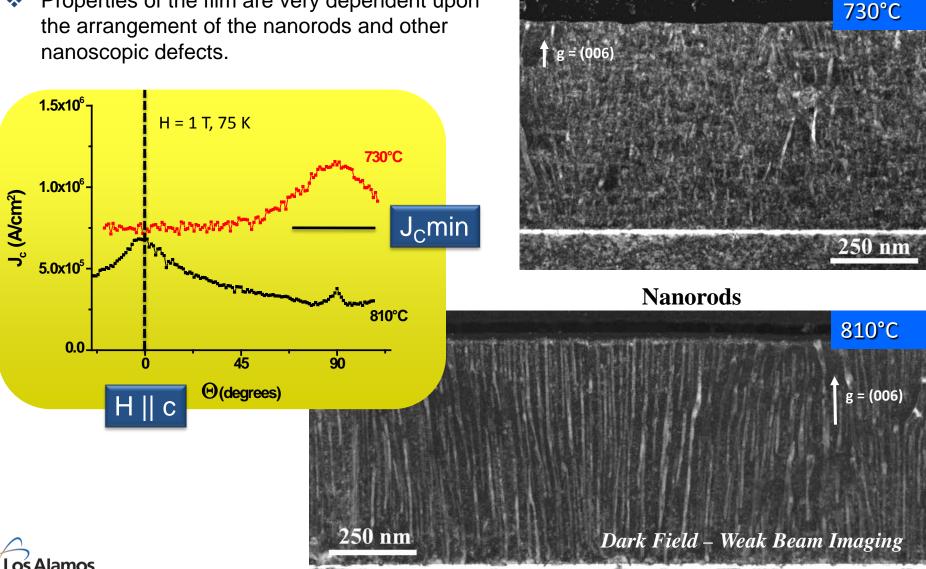
[010] BYNO || [010] YBCO (400) BYNO || (200) YBCO





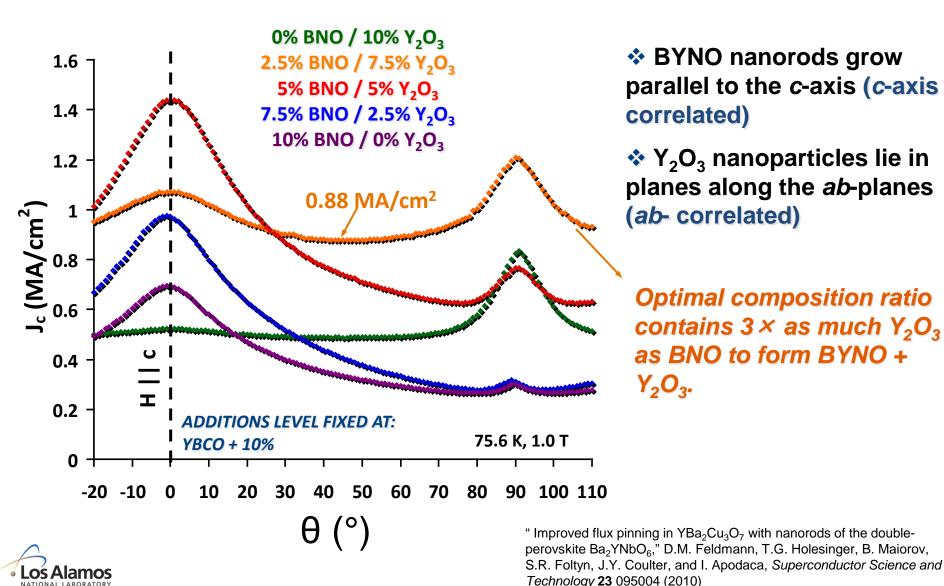
Self-assembly of the BYNO nanorods is temperature dependent.

Properties of the film are very dependent upon the arrangement of the nanorods and other



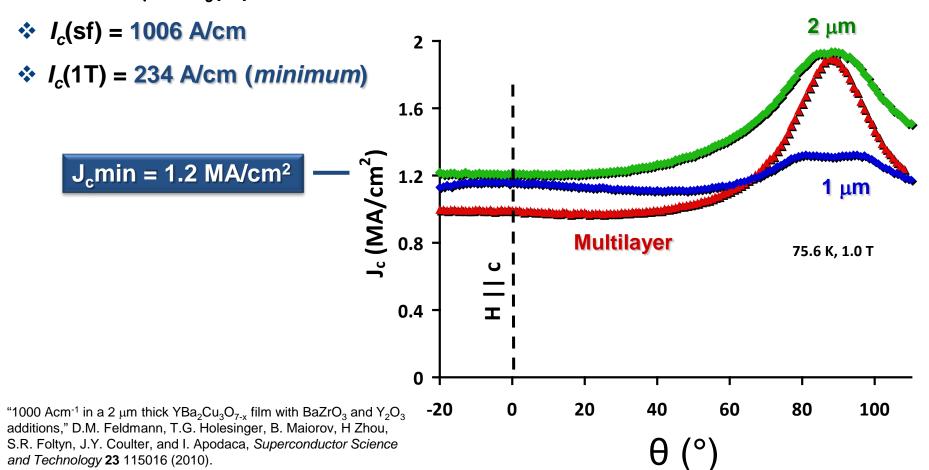
Nanorods and Nanoparticles

Engineered Performance with Targeted Second Phase Additions: Combining *c*-axis and *ab*- correlated structures



Best results to date are from a 2 μ m thick YBCO + BZO film.

- ❖ YBCO + 5 mol% BZO + 7.5 mol% Y₂O₃
- $t = 1.95 \mu m, J_c(sf) = 5.16 MA/cm^2$



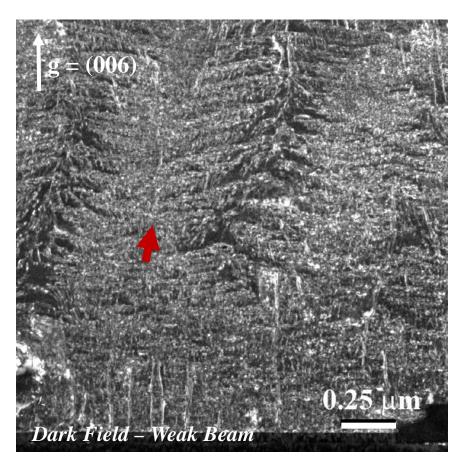


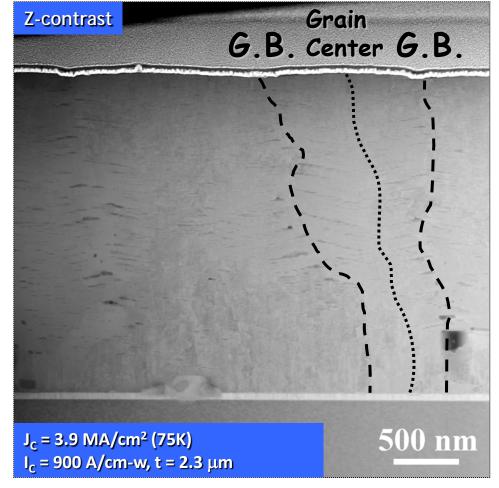
Film Synthesis and J_c Data from Matt Feldmann

The high J_C films have an ultra-fine defect structure with minimal grain boundary phases.

- Screw-dislocation mediated growth
- 2-D image of a 3-D structure!

Grain boundary phases (Y₂O₃) are minimized in this sample.





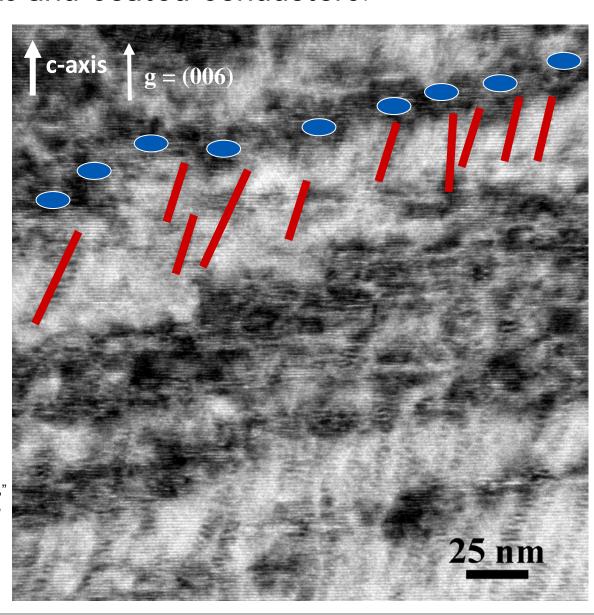


Nanorods and Nanodots: An Optimized Two-Defect Pinning Structure for REBCO Films and Coated Conductors.

- ❖ Y₂O₃ nano-particle layers
 - Tilted with respect to ab plane.
 - Symmetric about each grain's center.
 - TEM imaging of strain within the film is associated with the Y₂O₃ nanoparticles.
- Short, truncated BZO nanorods
 - Tilted relative to film normal;
 - Symmetric about each grain center. (splay)

[&]quot;Synergetic combination of different types of defects to optimize pinning landscape using BaZrO₃-doped YBa₂Cu₃O₇," Maiorov, B., Baily, S.A., Zhou, H., Ugurlu, O., Kennison, J.A., Dowden, P.C., Holesinger, T.G., Foltyn, S.R., Civale, L., *Nature Materials* **8** 398-404 (2009).

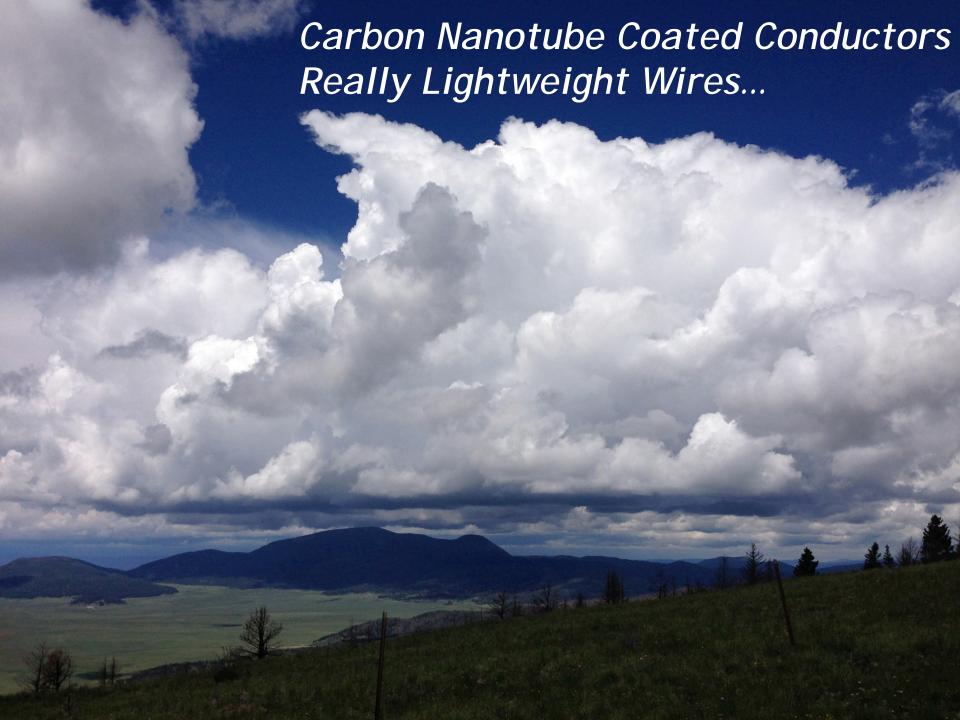




Part I Summary - HTS Conductors

- HTS wires are highly engineered composite materials. (HTS layer is only about 2% of the cross section.)
- For HTS wires to work at the km length scale....
 - Alignment micron-sized grains for high inter-grain currents requiring singlecrystal-like substrates by the kilometer.
 - Nano-engineered defect structures for high intra-grain J_C.
 - High-rate, robust manufacturing.
- Trade-offs are made between the best film processes and those that can work in an industrial environment.
- HTS wires are finally reaching the commercial stage with applications in grid security and reliability in city centers.
 - 1986 Bednorz and Mueller and cuprate superconductivity
 - 2014 ComEd / AMSC's Chicago "Resilient Electric Grid" project





Acknowledgements







- * CNT Coated Conductors Laboratory Industry Collaboration
 - Synthesis and Characterization Raymond Depaula, Pallas Papin, John Rowley, Terry Holesinger
 - Industry Oversight (Chevron) Steve Andre, Keith Sperling, Ben Bloys
 - RPSEA James Pappas
 - Laboratory Liaison Susan Brockway,
 - LANL Chevron Fellow Don Hickmott

Funding for this project is provided by RPSEA through the "Ultra-Deepwater and Unconventional Natural Gas and Other Petroleum Resources" program authorized by the U.S. Energy Policy Act of 2005 and from Chevron.

RPSEA (<u>www.rpsea.org</u>) is a nonprofit corporation whose mission is to provide a stewardship role in ensuring the focused research, development and deployment of safe and environmentally responsible technology that can effectively deliver hydrocarbons from domestic resources to the citizens of the United States. RPSEA, operating as a consortium of premier U.S. energy research universities, industry, and independent research organizations, manages the program under a contract with the U.S. Department of Energy's National Energy Technology Laboratory.



Advanced Conductor Development for Today's Challenging Applications

CNT Coated Conductors: Development of a lightweight, high-conductivity wire technology based on carbon nanotubes.







CNT Coated Conductors

Replacing the 19 miles of Cu wire and cables on the F-35 joint strike fighter with CNT wire would save 1,935 lbs.





Initial Funding: Chevron /RPSEA for ultra-deep water oil recovery.

CNT Coated Conductors: Lightweight Wire Roadmap

- Large-Scale Manufacturing: Solution Coating and Wire Drawing
 - Flexible coating process enabled with CNT solutions.
 - Range from full dissolution to suspended fibers.
 - Allows for control and manipulation of large quantities of CNTs.
 - High-pressure alignment and densification with wire drawing

Targets

- Conductivity on par with or better than pure Cu forms.
- 1/3 to 1/4 the density of a pure copper wire.
- High specific conductivity (> 2x Cu)
- Targeted wire sizes: 32 10 AWG
- High Strength, High thermal conductivity.
- ❖ End Product: A Base Material for wires and cables for a range of applications involving: lightweighting, energy efficiency, structural support, corrosion resistance, and thermal management.



CNTs for Advanced Conductor Development

- Extraordinary electrical, mechanical and thermal properties.
- Room temperature operation
- Conductivity / Current Capacity of Individual CNTs are substantially better than copper.
 - Conductivities 1000 times higher than Cu.
 - Tensile strength up to 100 times greater than steel
 - Thermal conductivity up to 10 times greater than Cu.

Issues for Development

Need aligned, closely packed CNTs.

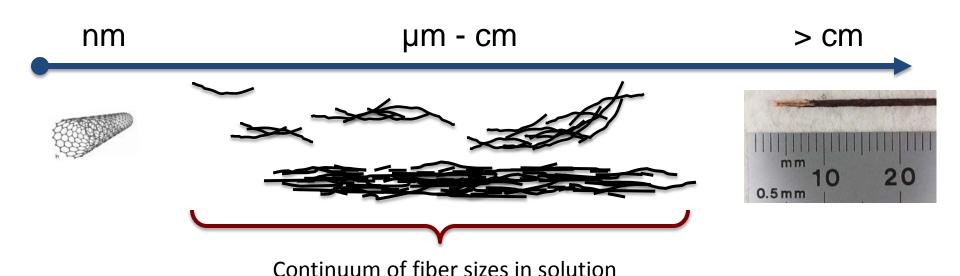
Technology scale is 3 to 6 orders of magnitude larger than the individual CNTs.

Technology has to be amenable to the production floor.



Nanotubes to Wires: Manufacturing at the Mesoscale.

- Question: How do you take nanotubes and manufacture technology scale devices that are 3-6 orders of magnitude larger?
- Approach: Develop an intermediate building block.
 - Carries the CNT alignment
 - Functionalized
 - Malleable for the assembly process





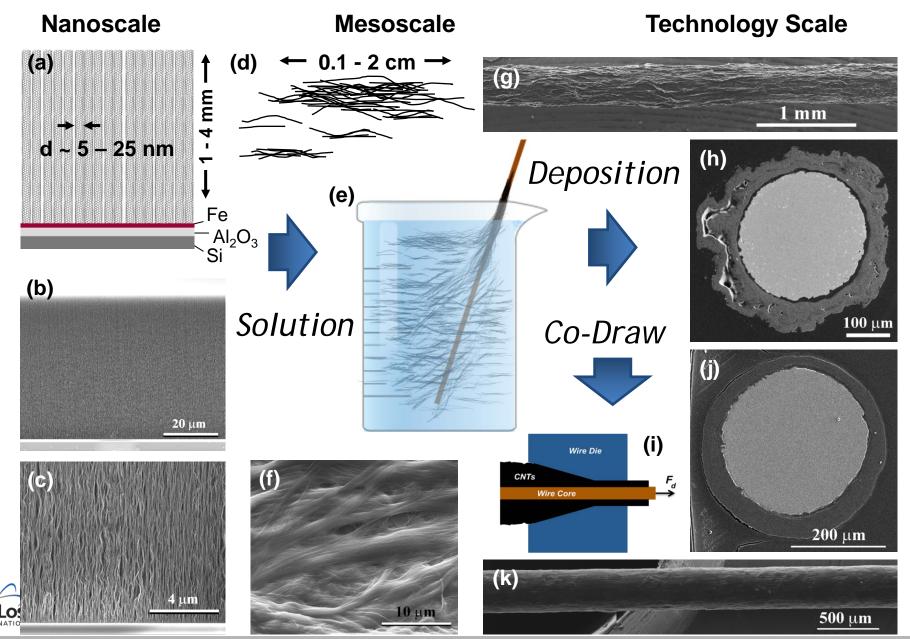
Solution Deposition (Dip Coating) and Wire Drawing for CNT Composite Development.

- Solutions: Not driving for full dissolution of individual CNTs.
 - Acid (Sulfuric) Based:
 - Water Based: Triton X / SDS / Dawn
- Preference for sulfuric-based solutions.
 - Better control of fibers in solution
- Base material: forest-grown multiwall CNTs
 - Long length (mm scale)
 - High-purity

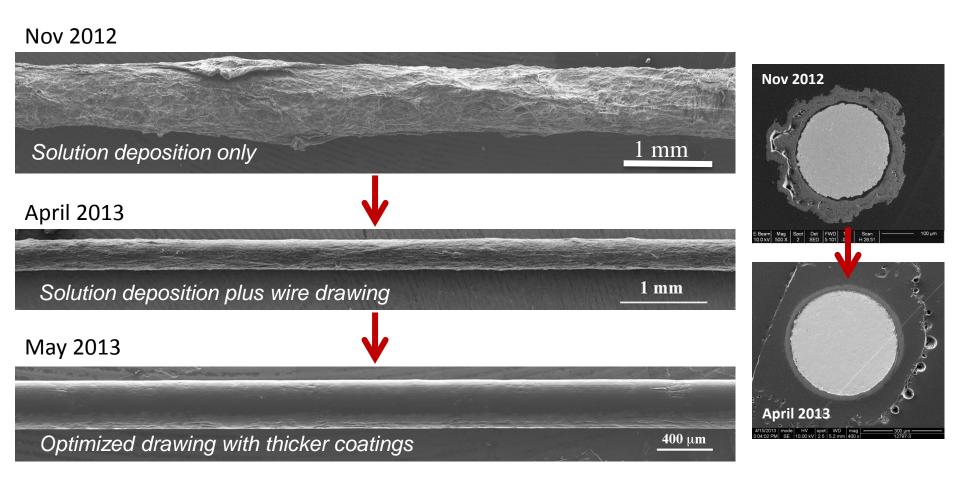
- Solution allows for addition of other materials.
 - SWNTs, DWNTs
 - Metal infiltration (particles / salts)
- Mechanical bond between CNTs and wire former.
 - Abraded prior to coating
 - CNT green coat ≈ 1 to 2 mm thick.
 - Drawn in the wet state and dried ≈ 10 to 90 µm.



Laboratory scale processing of CNT composite conductors.



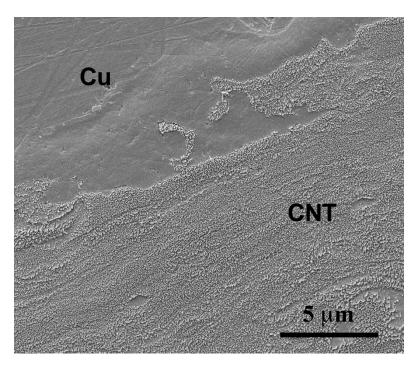
Combination is needed to produce thick, dense, and aligned CNT coatings about a wire former.





Mechanical Bonding between CNTs and Cu

Use the wire drawing steps to embedded the CNTs into the abraded Cu.





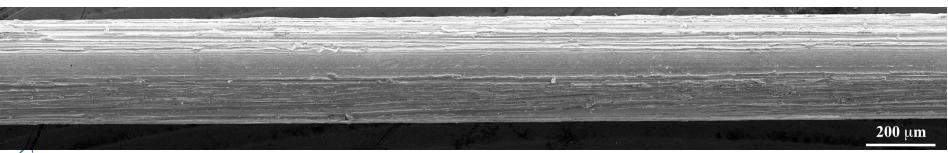
As-Received 28 AWG Cu wire

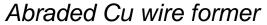
R/L (Ω/cm)	Core ρ (μΩ-cm)
2.21E-03	1.78

Abraded 28 AWG Cu wire

University of New Mexico - Nov. 2015

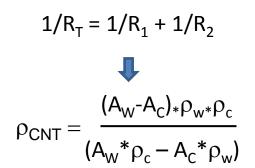
R/L (Ω/cm)	Core ρ (μΩ-cm)
2.36E-03	1.80

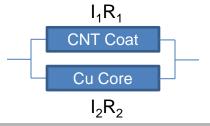




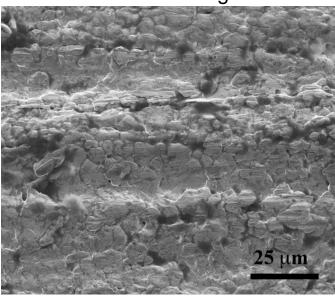
Electrical Measurements

- Parallel-resistor model to determine the resistivity of the CNT coatings.
 - Laser micrometer for dimensional measurements.
 - 4-probe pressed contacts onto the CNT coating.
- Measurement of the Cu core has to come after removal of CNT coating.









CNT coated wire

R/L	Wire ρ	CNT ρ	Coating	CNT
(Ω/cm)	(μΩ-cm)	(μΩ-cm)	(µm)	% x-sec
2.34E-03	2.46	13.1	32.4	27.0%

Cu Core CNTs Removed

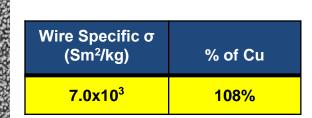
R/L (Ω/cm)	Core ρ (μΩ-cm)
2.46E-03	1.89

 A_W = x-sec area of wire¹ A_C = x-sec area of core¹ ρ_W = measured resistivity of whole wire ρ_C = measured resistivity of bare substrate²

Cross-sectional SEM analysis shows the aligned CNT structure within a high-conductivity coating.

CNT Particulate

5:1 Commercial DWNTs: LANL MWNTs



100 µr

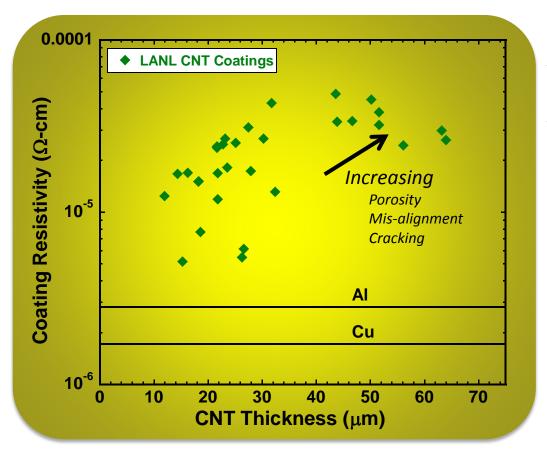
CNT coated wire

R/L	Wire ρ	CNT ρ	Coating	CNT
(Ω/cm)	(μΩ-cm)	(μΩ-cm)	(µm)	% x-sec
2.31E-03	2.17	5.5	26.3	28.1%

Cu Core CNTs Removed

R/L (Ω/cm)	Core ρ (μΩ-cm)
2.60E-03	1.76

Summary of CNT Coating Performance



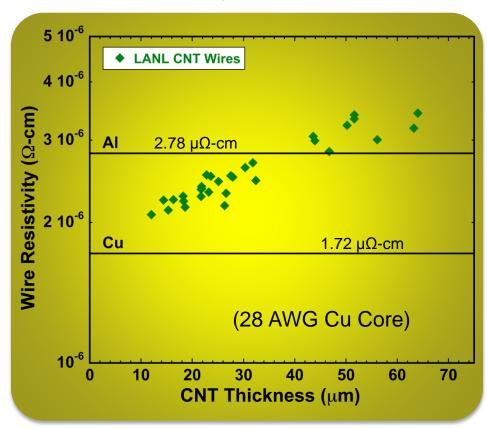
- CNT coating performance is approaching Cu.
- Additional optimization of the drawing and coating processes is needed.
 - Remove residual porosity and further improve alignment with the thicker coatings.
 - Limit number of current-limiting defects.
 - Likely need better functionalization between CNTs.



Summary of CNT Wire Performance

- With increasing coating thickness, the overall composite resistivity increases.
- For comparable behavior to Cu, obvious need to keep improving CNT coating performance.

Wire Resistivity vs. CNT Thickness



Wire $\rho = 2.12 \,\mu\Omega$ -cm; CNT coating $\rho = 5.5 \,\mu\Omega$ -cm

500 μm



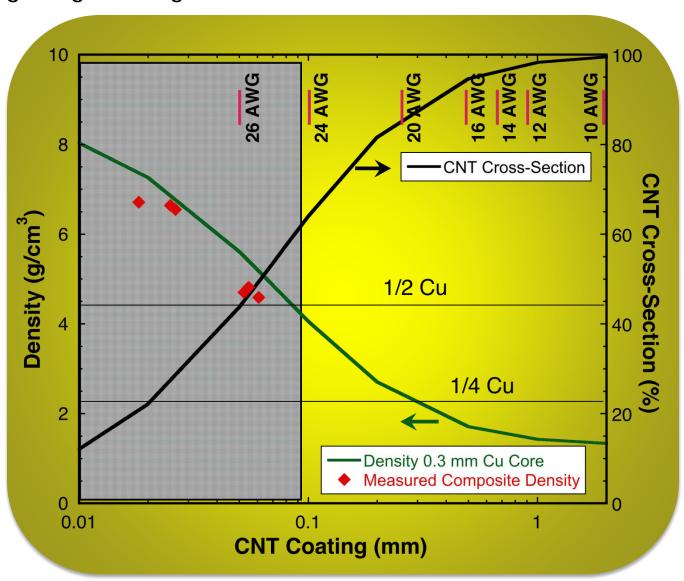
Calculations of composite density give us an idea of how close we are to achieving a light-weight wire.

- Calculated density Green curve
- Measured density –
 Red diamonds
- Have reached coatings of 90 microns (gray area)
- ❖ Wires with < ½ the density of Cu.</p>

Metals

Cu - 8.96 g/cm³

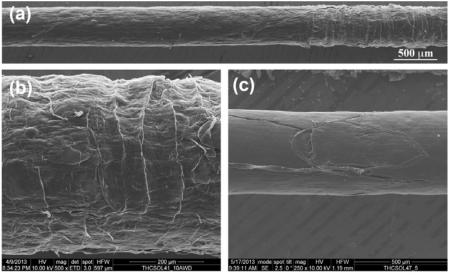
AI - 2.70 g/cm³



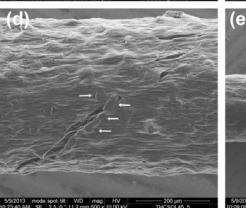


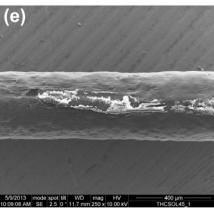
Understanding Current Limiting Mechanisms to Improve Performance.

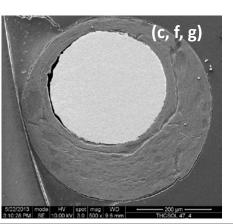
- * Focus on microscopy for understanding "good" or "bad" performance.
 - Structure-property correlations
 - Feedback loop for process modifications



- a) Sheath failure during drawing
- b) Sheath failure during drawing
- c) Crack development during coating
- d) Particle induced cracking
- e) Embedded particles.
- f) Non-uniform coatings.
- g) Coating separation from substrate.



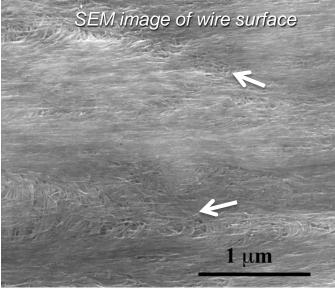




There are variations in density along and across the CNT coatings.

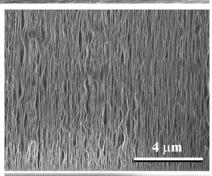
Room for further improvement in the density of the coatings.

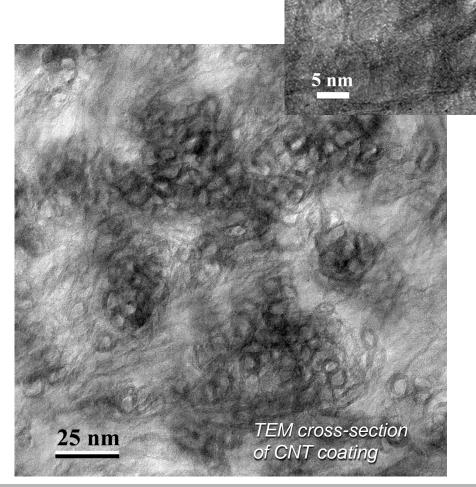
May be limitations due to wavy nature of the forest grown CNTs.



SEM crosssection of CNT forest





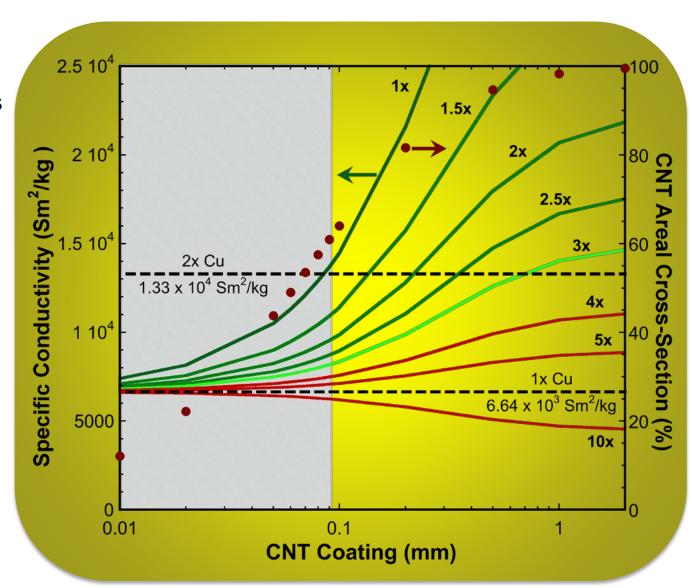


TEM cross-section

of CNT bundle

What would it take to obtain a CNT Coated Conductor with a specific conductivity of 2 x copper?

- 0.3 mm Cu core.
- Calculate specific σ's based on several CNT coating (ρ) performance levels.
- For 2x specific σ relative to Cu?
 - ½ conductivity of Cu
 - 200 micron coating
 - ◆ 28 → 22 AWG





CNT Coated Conductors with Commercial Base-Material CNTs

- CNT coating on 28 AWG Cu wire
- Wire density: 5.3 g/cm³
- CNT coating ρ: 46 μΩ-cm
- Quick demonstration to show ability to use commercial sources for CNTs.

Composite wire

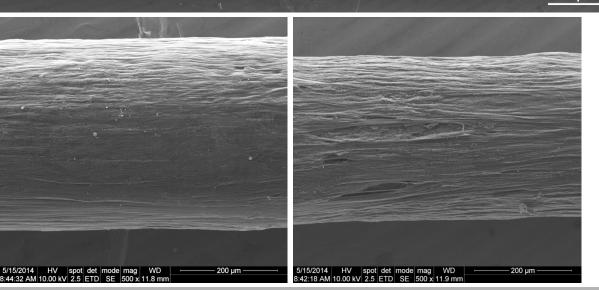
R/L	Wire ρ	_	Coating	CNT
(Ω/cm)	(μΩ-cm)		(µm)	% x-sec
2.47E-03	2.57	46.1	28.7	29.1%

Cu Core after CNTs removed

R/L (Ω/cm)	Wire ρ (μΩ-cm)
2.51E-03	1.85

Initial wires limited by non-uniformity in the coating

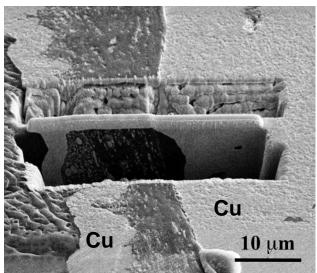


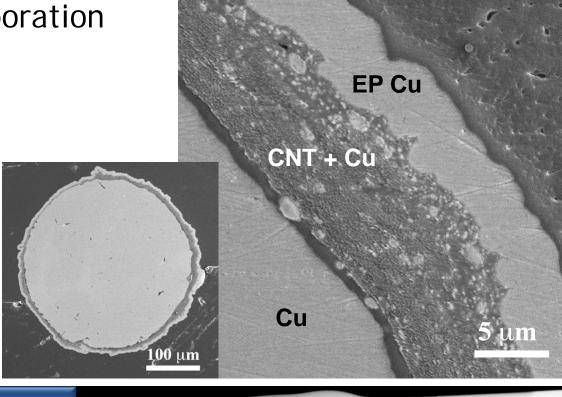


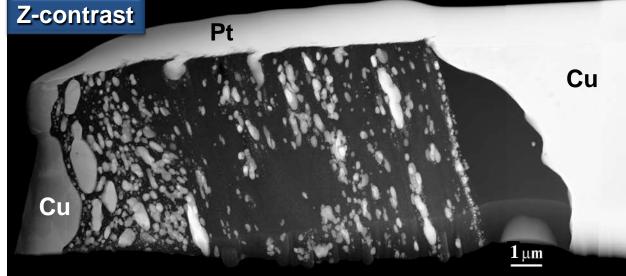
400 µm

Electroplating / Cu incorporation

- Initial work to demonstrate processes that may be needed for specific applications.
- Cu incorporation with Cu-salt addition to solution plus anneal.
- Cu electroplating to demonstrate continuous coating.



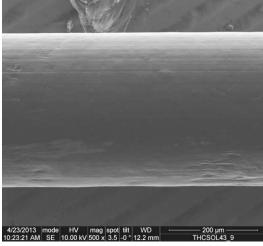


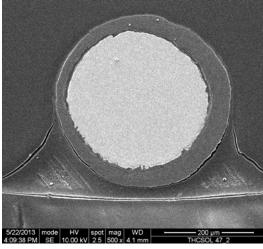




Summary - Carbon Nanotube Coated Conductors

- Highly-aligned, thick CNT coatings on Cu (and other wire formers) with industrially-scalable processes.
 - Solution deposition
 - Wire drawing
- Alignment Across Scale: Alignment of nm sized materials at the macroscale (mm).
 - **CNT Forests**
 - Extended Fibers in solution
 - Wire drawing to finish assembly
- High Performance Wires.
 - Best result: 5.5 $\mu\Omega$ -cm
 - Most CNT coatings in range of 10 to 100 $\mu\Omega$ -cm.
 - Specific conductivities that now exceed Cu.
 - Focus on eliminating manufacturing defects.
- Opportunity to further improve properties with better functionalization of the CNTs.







Holesinger et al, PCT application and Paper in Preparation 2015.

Path Forward

- Need to move to reel-to-reel continuous coating and wire drawing.
 - Uniformity
 - Application Testing
- Final product form
 - Protective coatings
 - Insulation
- Move out of laboratory
 - PCT filed; available for view
 - Work with Industrial partners to identify application pulls



Commonality in Advanced Conductor Development: Mesoscale Science.

- Imagine the ability to manufacture at the mesoscale...
- ... directed assembly of mesoscale structures that possess unique functionality...
- ... bottom-up design with nanoscale (nanoengineered) functional units producing next-generation technological innovation.

This is the promise of mesoscale science.

FROM QUANTA TO THE CONTINUUM: OPPORTUNITIES FOR MESOSCALE SCIENCE

A Report from the Basic Energy Sciences Advisory Committee U.S. Department of Energy September 2012

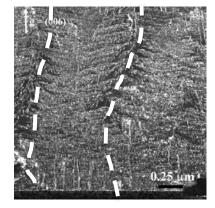
Key Concept: Conducting Research within the Context of Scalable Processing.



Mesoscale Science of Advanced Conductor Development

Mesoscale Building Block

Nanoengineered YBCO grain



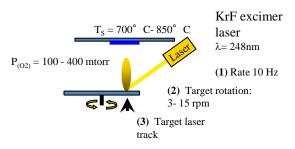
CNT Fiber in Solution Building Block



Continuum of fiber sizes in solution

Bottom Up Synthesis and Alignment of Mesoscale Structures

Hetero Epitaxial Growth Single-Crystal like Substrates



Grapho-Epitaxial CNT Synthesis Solution Deposition & Wire Drawing

